

945.638



# PATENT SPECIFICATION

NO DRAWINGS

945.638

Date of Application and filing Complete Specification: Oct. 2, 1962.

No. 37281/62.

Application made in Germany (No. B64238 IVa/46c<sup>4</sup>) on Oct. 4, 1961.

Complete Specification Published: Jan. 2, 1964.

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Index at acceptance:—Class C4, XI.

International Classification:—F 25 h.

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are ROLAND SCHWEN and WILHELM MUENSTER, citizens of Germany and residents, respectively of 56 Saarlandstrasse, Ludwigshafen/Rhein, Germany; and 9 Saarbrueckener Strasse, Ludwigshafen/Rhein, Germany.

## COMPLETE SPECIFICATION

### Preventing Corrosion by Antifreeze Agents

WE ROLAND SCHWEN and WILHELM MUENSTER, citizens of Germany, hereby declare that we have invented a process for preventing corrosion by means of antifreeze agents in aqueous solutions of calcium ions.

PATENTS ACT, 1949

SPECIFICATION NO. 945,638

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 23rd day of September 1964 this Specification has been amended under Section 29 in the following manner:—

Page 6, before "WHAT WE CLAIM IS:—", insert "Having regard to the provisions of Section 9 of the Patents Act, 1949, attention is drawn to the claims of Patent No. 811,675".

THE PATENT OFFICE,  
17th November, 1964

D 30689/1 (1)/R.109 200 11/64 PL

25 molybdates, aliphatic, alicyclic or heterocyclic amines and sodium carbonate. They are conventionally used in a combination of one to three, sometimes even more than three, compounds to prevent corrosion by antifreeze agents, but they still have considerable defects. Thus for example antifreeze agents containing phosphorus are very sensitive to metal ions, other than alkali metal ions, because the  
30 phosphates are precipitated and may lead to stoppages in the cooling system. Antifreeze agents which contain arsenates, molybdates and tungstates as corrosion inhibitors behave similarly.  
35 Antifreeze agents containing amines attack copper and its alloys. Sodium mercaptobenzothiazole is therefore often added thereto. Such combinations however do not give clear solutions but tend to form precipitates after some  
40 time owing to hydrolysis and ageing.

Attempts have already been made to keep

solely by accumulating corrosion inhibitors, but that rather it is often the case in practice that good properties already achieved are lost again upon the addition of further components. It is particularly difficult to develop an inhibitor combination which will give good results under varying conditions and not only with a single test and with only one kind of water.

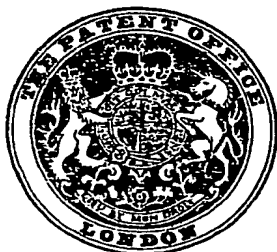
We have now found that corrosion by aqueous antifreeze agents is substantially prevented when the antifreeze agent is a 1,2-diol together with the following percentages by weight, with reference to the 1,2-diol, of the following substances: 0.2 to 2%, preferably 0.5 to 1% of borax, 0.1 to 1%, preferably 0.2 to 0.4% of sodium nitrate, 0.1 to 1%, preferably 0.2 to 0.4% of sodium nitrite, 0.01 to 0.1%, preferably 0.02 to 0.04% of sodium silicate, 1 to 4%, preferably 1.5 to 2.5% of sodium benzoate, and 0.01 to 0.5%, preferably 0.05 to 0.2% of benzotriazole. The

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## COMPLETE SPECIFICATION

### Preventing Corrosion by Antifreeze Agents

We, BADISCHE ANILIN-& SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of Ludwigshafen/Rhine, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that aqueous antifreeze agents cause corrosion phenomena in piping systems. For this reason corrosion inhibitors are added to such antifreeze agents. Such corrosion inhibitors include for example borax, sodium dichromate, sodium mercaptobenzothiazole, sodium silicate, potassium or sodium phenylamino acetate, alkaline earth metal borates, triethanolamine, alkali metal and ammonium salts of phosphoric acid and of polycondensed phosphoric acids, benzotriazole, alkali metal arsenites, alkali metal arsenates, alkali metal molybdates, aliphatic, alicyclic or heterocyclic amines and sodium carbonate. They are conventionally used in a combination of one to three, sometimes even more than three, compounds to prevent corrosion by antifreeze agents, but they still have considerable defects. Thus for example antifreeze agents containing phosphorus are very sensitive to metal ions, other than alkali metal ions, because the phosphates are precipitated and may lead to stoppages in the cooling system. Antifreeze agents which contain arsenates, molybdates and tungstates as corrosion inhibitors behave similarly.

Antifreeze agents containing amines attack copper and its alloys. Sodium mercaptobenzothiazole is therefore often added thereto. Such combinations however do not give clear solutions but tend to form precipitates after some time owing to hydrolysis and ageing.

Attempts have already been made to keep

calcium ions in solution by means of polyphosphates. Polyphosphates have the disadvantage however that in the course of time they hydrolyse and thus lose their activity.

Antifreeze agents with a content of sodium benzoate and sodium nitrite have the disadvantage that they have only a low buffer capacity and consequently are very sensitive to acid oxidation products of ethylene glycol and to water having an acid reaction.

Although this disadvantage does not occur when inhibiting corrosion by means of borax, antifreeze agents inhibited with borax have the disadvantage that the corrosion inhibiting effect is dependent to a more pronounced degree on the working conditions than in the case of the previously mentioned antifreeze agents.

It is known to the expert that weaknesses of individual inhibitors cannot be obviated solely by accumulating corrosion inhibitors, but that rather it is often the case in practice that good properties already achieved are lost again upon the addition of further components. It is particularly difficult to develop an inhibitor combination which will give good results under varying conditions and not only with a single test and with only one kind of water.

We have now found that corrosion by aqueous antifreeze agents is substantially prevented when the antifreeze agent is a 1,2-diol together with the following percentages by weight, with reference to the 1,2-diol, of the following substances: 0.2 to 2%, preferably 0.5 to 1%, of borax, 0.1 to 1%, preferably 0.2 to 0.4% of sodium nitrate, 0.1 to 1%, preferably 0.2 to 0.4% of sodium nitrite, 0.01 to 0.1%, preferably 0.02 to 0.04% of sodium silicate, 1 to 4%, preferably 1.5 to 2.5% of sodium benzoate, and 0.01 to 0.5%, preferably 0.05 to 0.2% of benzotriazole. The

sodium ion in one or more of the sodium compounds may be replaced partly or wholly by one or more other alkali metal or ammonium ions. If equivalent ammonium salts are used, it is advantageous to add a further component, for example sodium mercaptobenzothiazole in amounts of 0.1% to 1% by weight, to protect copper-containing alloys.

It is moreover advantageous to add to the antifreeze concentrates containing the said compounds, one or more compounds which increase the resistance to ageing, for example phenylglycine potassium salt, phenylglycine sodium salt, aminocarboxylic acids, such as glyccoll, alanine, or isatic acid, isatin or cyclic glycol carbonates derived for example from ethylene or propylene. If desired, aliphatic alcohols, amines and aqueous antifreeze agents based on 1,2-diols, which contain the said combination as corrosion inhibitors, may be used in cooling systems which are composed of a great variety of metals or metal alloys.

As may be seen from the following Examples, water of greatly varied composition may be used for diluting the antifreeze agent concentrates without the corrosion inhibition of the coolant being affected. This is more surprising because it is known that the influence of different kinds of water on the inhibiting and corrosive properties of an inhibitor combination is very great and that often the desired improvement cannot be achieved by combining individual compounds having corrosion inhibiting properties. Often the corrosion inhibition is worsened.

The superiority of the combinations according to this invention over the compounds hitherto used for corrosion inhibition may be seen from the following experiments.

The tests were carried out according to ASTM specifications (ASTM D 1384—55 T, published by the American Society for Testing

Materials, 1955) or by the method of Eidgenössische Materialprüfungs- und Versuchsanstalt für Industrie, Bauwesen und Gewerbe, Zürich (hereinafter referred to as EMPA), published in "Schweizer Archiv für angewandte Wissenschaft und Technik", 22, pp. 65—74, March 1956. 1 part by volume of antifreeze agent concentrate is diluted with 2 parts by volume of the following kinds of water:—

1. distilled water,
2. Ludwigshafen drinking water,
3. distilled water at 10° German hardness, hardened according to DIN 53902,

4. synthetic lime water at 20° German hardness (140 mg of highest-purity calcium oxide are dissolved with carbon dioxide in 800 ml of distilled water, 4 ml of solution A and 2 ml of solution B, prepared according to DIN specification 53902, are added and the whole is made up to 1000 ml with distilled water).

The following abbreviations are used:— The corrosion values (denoted by K in the Examples) are given in the decrease in weight per sq. cm. rounded off to the nearest mg. Values of less than 0.5 are regarded as very good and values below 1 as good. Values less than 1 are therefore in general not given individually, although in all tests all the metals mentioned in the text were tested. The indices following the letter K indicate the metal or alloy to which the value applies.

The following metals and alloys were tested:—Cu copper; br brass; RB red-brass; SS soft solder; GCI grey cast iron; II ingot iron (soft steel); Al pure aluminium; Sil Silumin (an aluminium alloy containing silicon); CAI cast aluminium.

Percentages in the Examples are by weight and parts are parts by volume.

#### EXAMPLE 1

1 part of ethylene glycol, inhibited with 1% of borax, 0.3% of sodium nitrate, 0.35% of sodium nitrite, 2.25% of sodium benzoate, 0.03% of sodium silicate and 0.07% benzotriazole, is diluted with 2 parts of water:—

No of water according to ASTM:—

1	2	3	4
K is less than 1 for all samples	K SS = 1 K is 0.2 or less for all other samples	K is less than 1 for all samples	K SS = 1 K is 0.2 or less for all other samples

No of water according to EMPA

1	2	3	4
K is less than 1 for all samples	K is less than 0.3 for all samples	K is less than 0.6 for all samples	K is less than 0.2 for all samples

## EXAMPLE 2

1 part of 1,2-propylene glycol, inhibited with 0.5% of borax, 0.3% of sodium nitrate, 0.35% of sodium nitrite, 2.25% of sodium benzoate, 0.03% of sodium silicate and 0.07% of benzotriazole, is diluted with 2 parts of water,

Water No (ASTM)	1	2	3	4
	K SS = 1 K is less than 0.1 for all other samples	K is less than 0.8 for all samples	K is less than 0.7 for all samples	K is less than 0.8 for all samples

Water No (EMPA)	1	2	3	4
	K SS = 1 K is less than 0.2 for all other samples	K is less than 0.2 for all samples	K is less than 0.2 for all samples	K is less than 0.1 for all samples

## EXAMPLE 3

1 part of ethylene glycol, inhibited with 1% of borax, 0.3% of sodium nitrate, 0.35% of sodium nitrite, 2.25% of sodium benzoate, 0.03% of sodium silicate, 0.07% of benzotriazole and 0.2% of isatin, is diluted with 2 parts of water:—

Water No (ASTM)	1	2	3	4
	K SS = 1 K is less than 0.2 for all other samples	K is less than 0.8 for all samples	K is less than 0.5 for all samples	K is less than 0.8 for all samples

Water No (EMPA)	1	2	3	4
	K SS = 1 K is less than 0.3 for all other samples	K is less than 0.2 for all samples	K is less than 0.4 for all samples	K is less than 0.2 for all samples

## EXAMPLE 4

1 part of ethylene glycol, inhibited with 2% of benzoic acid, 1% of cyclohexylamine, 0.9% of 30% caustic soda solution, 0.3% of sodium nitrate, 0.3% of sodium nitrite, 0.1% of benzotriazole, 0.03% of sodium silicate, 1% of borax, 0.1% of 1,2-propylene glycol carbonate, 0.1% of isatin and 0.5% of tridecanol, is diluted with 2 parts of water:—

Water No (ASTM)	1	2	3	4
	K is less than 0.5 for all samples	K is less than 0.5 for all samples	K is less than 0.3 for all samples	K is less than 0.5 for all samples

Water No (EMPA)	1	2	3	4
	K is less than 0.3 for all samples	K is less than 0.7 for all samples	K is less than 0.1 for all samples	K is less than 0.3 for all samples

## EXAMPLE 5

1 part of ethylene glycol, inhibited with 0.5% of borax, 0.2% of a mixture of the sodium and potassium salts of phenyl glycine, 0.3% of sodium nitrate, 0.35% of sodium nitrite, 2.25% of sodium benzoate, 0.07 of benzotriazole, 0.5% of tridecanol and 0.03% of sodium silicate, is diluted with 2 parts of water:—

Water No (ASTM)	1	2	3	4
	K SS = 0.7 K is less than 0.1 for all other samples	K is less than 0.6 for all samples	K SS = 0.8 K is less than 0.2 for all other samples	K is less than 0.6 for all samples

Water No (EMPA)	1	2	3	4
	K is less than 0.5 for all samples	K is less than 0.6 for all samples	K is less than 0.4 for all samples	K is less than 0.8 for all samples

## EXAMPLE 6

1 part of ethylene glycol, inhibited with 0.5% of borax, 0.2% of a mixture of the sodium and potassium salts of phenyl glycine, 0.3% of sodium nitrate, 0.35% of sodium nitrite, 2.25% of sodium benzoate, 0.07% of benzotriazole, 0.03% of sodium silicate and 0.2% of 1,2-propylene glycol carbonate, is diluted with 2 parts of water:—

Water No (ASTM)	1	2	3	4
	K is less than 0.6 for all samples	K is less than 0.6 for all samples	K is less than 0.4 for all samples	K is less than 0.4 for all samples

Water No (EMPA)	1	2	3	4
	K is less than 0.6 for all samples	K is less than 0.4 for all samples	K is less than 0.4 for all samples	K is less than 1 for all samples

The following tests A to D are given for purposes of comparison:—

## A

1 part of ethylene glycol, which contains 2.5% of borax, is diluted with 2 parts of water:—

Water No (ASTM)	1	2	3	4
	K is less than 0.3 for all samples	K II = 2 K GCI = 7 K CAI = 4	K II = 9 K GCI = 7 K CAI = 6	K II = 4 K GCI = 11 K CAI = 2

Water No (EMPA)	1	2	3	4
	K SS = 4	K II = 2 K AI = 3	K AI = 10	K GCI = 12 K AI = 9 K Sil = 1

## B

1 part of 1,2-propylene glycol, inhibited with 2.5% of borax, is diluted with 2 parts of water:—

Water No (ASTM)	1	2	3	4
	K is less than 0.2 for all samples	K II = 2 K GGI = 5 K Cal = 7	K Cal = 15	K GCI = 8 K Cal = 7

Water No (EMPA)	1	2	3	4
	K is less than 0.2 for all samples	K II = 11 K GGI = 26 K AI = 7	K II = 15 K GGI = 24 K AI = 3 K Sil = 7	K is less than 0.1 for all samples

## C

1 part of ethylene glycol, inhibited with 3.7% of triethanol ammonium phosphate and 0.25% of sodium mercaptobenzothiazole, is diluted with 2 parts of water:—

Water No (ASTM)	1	2	3	4
	K is less than 0.1 for all samples	K II = 2 K GGI = 2 K Al = 1	K is less than 0.1 for all samples	K II = 2 K GGI = 3

Water No (EMPA)	1	2	3	4
	K is less than 1 for all samples	K GCI = 1	K II = 2 K GCI = 1 K Al = 5	K II = 4 K GCI = 3 K Al = 4 K Sil = 2

## D

1 part of ethylene glycol, inhibited with 5% of sodium benzoate and 0.5% of sodium nitrite, is diluted with 2 parts of water:

Water No (ASTM)	1	2	3	4
	K SS = 1	K is less than 0.4 for all samples	K SS = 1	K is less than 0.5 for all samples

Water No (EMPA)	1	2	3	4
	K SS = 1	K SS = 3	K SS = 3	K Cu = 1 K RB = 1 K Sil = 1

## WHAT WE CLAIM IS:—

1. An aqueous antifreeze agent comprising one or more 1,2-diols together with the following percentages by weight (all with reference to the diol or diols) of the following substances: 0.2 to 2% of borax, 0.1 to 1% of sodium nitrate, 0.1 to 1% of sodium nitrite, 0.01 to 0.1% of sodium silicate, 1 to 4% of sodium benzoate and 0.01 to 0.5% of benzotriazole.
2. An aqueous antifreeze agent as claimed in claim 1 comprising 0.5 to 1% of borax, 0.2 to 0.4% of sodium nitrate, 0.2 to 0.4% of sodium nitrite, 0.02 to 0.04% of sodium silicate, 1.5 to 2.5% of sodium benzoate and 0.05 to 0.2% of benzotriazole.
3. An aqueous antifreeze agent as claimed in claim 1 or 2 wherein the sodium ion in one

or more of the sodium compounds is partly or wholly replaced by one or more other alkali metal or ammonium ions.

4. An aqueous antifreeze agent as claimed in claim 3 which includes ammonium salts and also 0.1 to 1% by weight of sodium mercaptobenzothiazole when the agent is to be used in contact with copper-containing alloys.

5. An aqueous antifreeze agent as claimed in any of claims 1 to 4 which also contains one or more agents for improving resistance to ageing.

6. An aqueous antifreeze agent as claimed in any of claims 1 to 5 which also contains one or more aliphatic alcohols.

7. An aqueous antifreeze agent as claimed in any of claims 1 to 6 which also contains one or more amines.

8. Aqueous antifreeze agents substantially as described in any of the foregoing Examples 1 to 6.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

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